4.0 CONCEPTUAL MODEL OF MERCURY BEHAVIOR IN THE GUADALUPE RIVER WATERSHED

The conceptual model is presented in two parts. The first part summarizes, for a general audience, key aspects of mercury behavior in the Guadalupe River Watershed, based on an extensive review of the scientific literature and available site-specific data. Paired diagrams and technical explanations describe mercury transport, transformation, and bioaccumulation processes pertinent to the watershed. The second part of the conceptual model describes, in more detail, the key issues and essential information needed to support the development of a TMDL and Implementation Plan.

4.1 OVERVIEW OF MERCURY TRANSPORT PROCESSES

Most of the mercury in the Guadalupe River Watershed exists as relatively insoluble mercury sulfides in mine wastes that have accumulated in reservoir deltaic deposits and sediments, and in stream bottoms, banks, and flood plains. Mercury also exists adsorbed to sediment within the waterbodies. Mercury in dissolved form is a small fraction of the total mercury, although it may play a proportionally greater role in the formation of methylmercury. Because of the strong association of mercury with solids, the movement of mercury in the watershed is closely tied to the movement of sediments as described below.

4.1.1 TRANSPORT TO RESERVOIRS

During large runoff events, mercury-containing sediments (from mine wastes) are transported to the Guadalupe and Almaden Reservoirs in the historic mining areas (Figure 4-1). In these reservoirs, atmospherically deposited mercury is likely to be quantitatively less significant than the large mine-waste related influxes. In the two other reservoirs, Lexington and Calero, mercury inputs from atmospheric deposition or weathering of local minerals are likely more important. In the case of Calero, two

additional sources of mercury, can be cited: the transfers of water from Almaden Reservoir and from the Central Valley Project. For all four reservoirs, the non-atmospheric input of mercury is thought to be largely in particulate form, although a smaller fraction in dissolved form is more chemically reactive and thus on a per unit mass basis more likely to be methylated.
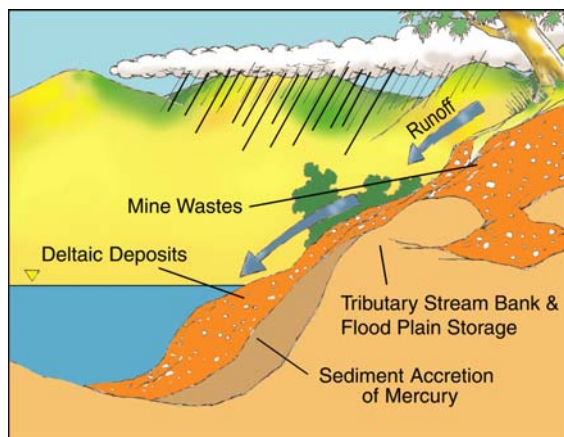

Figure 4-1. Transport to reservoirs.

4.1.2 CREEK/RIVER PROCESSES AT HIGH FLOW

During high flows, large loads of sediment-associated mercury are transported downstream in the creeks and in the Guadalupe River (Figure 4-2). In some reaches, bank erosion occurs to a greater extent than scouring of the bed sediments, and adds significantly to the total transport of mercury. A small percent of the total mercury load is transported as dissolved mercury or methylmercury. Drop structures along the tributary stream and the main stem of the Guadalupe River collect sediments, reducing further downstream transport.

4.1.3 CREEK/RIVER PROCESSES AT LOW FLOW

During low flow, the total flux of mercury in the creeks and river is much less (Figure 4-3). Transport of dissolved mercury is significant, but quantitatively small compared to the mercury transported as sediment during large storms. Sediment mercury transport is important when considering long-term effects of mercury in the watershed, although over the short-term dissolved mercury is more bioavailable. Even though some mercury may be methylated in creeks, Synoptic Survey data show that methylmercury concentrations decrease with travel distance in most stream reaches. In some reaches, the total mercury does increase with travel distance as the streams pass through areas with known mine-waste deposits.

4.2   OVERVIEW OF MERCURY TRANSFORMATION AND BIOLOGICAL UPTAKE

Because the toxicity of mercury to humans and wildlife is closely tied to its uptake through the food chain, it is important to understand the processes that transform mercury in water and sediments into more biologically active forms. Our best current

understanding of mercury transformations in reservoirs and creeks of the Guadalupe
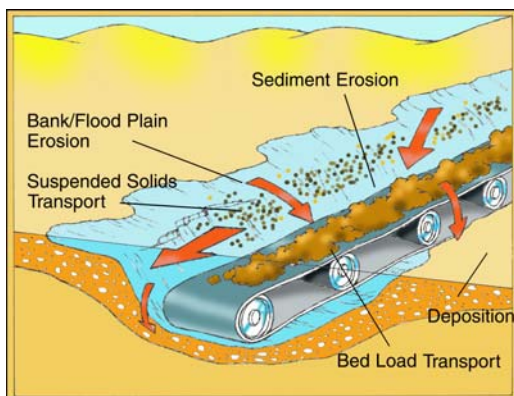River Watershed is summarized in the paragraphs which follow.
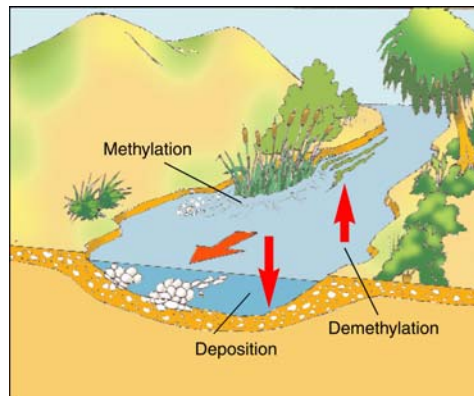

Figure 4-2. Creek/river processes at high flow.

Figure 4-3. Creek/river processes at low flow.

4.2.1 SUPPLY OF HG TO THE WATER COLUMN

Of the chemicals present in reservoirs, sulfides are most efficient at solubilizing
(weathering) mercury associated with particles (crystalline and amorphous HgS, and
adsorbed mercury) by forming aqueous mercury sulfide complexes (e.g., HgS^o,
$Hg(HS)_2^o$ (Paquette and Helz, 1997; Benoit et al., 1999). Evidence also exists that
organic ligands can enhance the solubility of solid-phase mercury (e.g. Ravichandran
et al., 1998). Mercury containing particles may be in the reservoir bottom sediments
or they may exist in suspension in the water column. Dissolved mercury that enters
the reservoirs with the wet-season runoff can also be a significant source. Data are
not available for this fraction, but total mercury flows, associated with large storm
events, particularly those immediately following other large events, can be very high
(e.g. several thousand ng/l).

4.2.2 DEVELOPMENT OF ANOXIC CONDITIONS IN RESERVOIR BOTTOM WATERS

During periods of stratification (summers), the lower waters of the reservoirs become
depleted of oxygen, and sulfate reducing bacteria (SRB) release sulfides (H_2S, HS^-)
into the water as a metabolic by-product (Figure 4-4). Concentrations of sulfides
increase in the lower reservoir waters particularly near the sediments. This process
also likely occurs in shallower water sediments along the reservoir edges and in
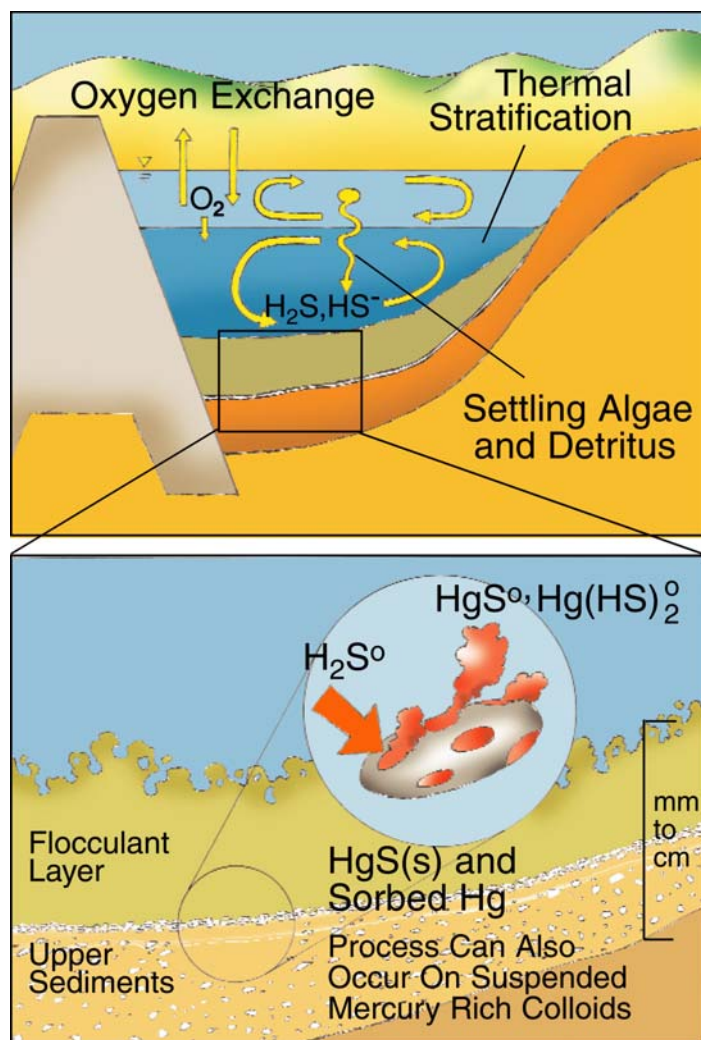streams with abundant aquatic vegetation.

Figure 4-4. A possible pathway for accelerated weathering of mercury solids.

4.2.3 MERCURY ALKYLATION

Although other bacteria have been shown to methylate mercury, it is the sulfate reducing bacteria (SRB) that are thought to be quantitatively the most important methylators.

Neutral mercury sulfide complexes are thought to readily enter these SRB (the same group producing the sulfides, Figure 4-5) as hypothesized by Benoit et al. (1999, 2001). Mercury may also enter SRB complexed with inorganic (Cl^- and OH^-) and small organic ligands, as hypothesized by many investigators (e.g. Golding et al., 2002 and Kelly et al., 2003). The SRB methylate this mercury in what is generally hypothesized to be a cometabolic (incidental) reaction (Compeau and Bartha, 1985). The accelerated weathering of mercury solids by sulfides and subsequent methylation

appears to be a significant means of bringing mercury into solution in these waters. Methylation can occur in the sediment or anywhere in the water column where sulfate reduction occurs and sulfides are thus present (e.g., Henry et al., 1995, Watras et al., 1995). Although bacteria have been extensively documented to methylate mercury, limited early data indicate that abiotic methylation can also be important (Gilmour et al., 2003; Lean and Siciliano, 2003).

4.2.4 UPTAKE OF METHYLMERCURY

The methylmercury produced diffuses from the SRB cells (probably complexed with sulfide). Much of the methylmercury produced is demethylated. However, a portion of the methylmercury enters algal cells at the base of the food chain (Figure 4-6). The methylmercury is thought to enter algal cells, neutrally complexed with small ligands, by passive diffusion. Although some investigators (e.g. Golding et al. 2002) have invoked active transport for uptake, passive diffusion rates appear to be greater than the actual methylation rates, thus indicating passive diffusion as more than adequate and not rate limiting (Hudson, R.J.M., personal communication)

4.2.5 BIOCONCENTRATION OF MERCURY

Methylmercury bioconcentrates as it moves up the food chain from algae to zooplankton to prey fish and to predator fish (Figure 4-7). The largest single jump in concentration occurs from the water to algae. Methyl mercury's biomagnification is among the largest of all known chemical compounds. Concentrations in fish can be millions of times higher than in water. The large degree of biomagnification is thought to result from methylmercury's strong affinity for thiols (sulfhydryl groups - SH) and sulfide and disulfide linkages ($R-S-R'$, $R-S-S-R'$) associated with proteins in organ and muscle tissue.
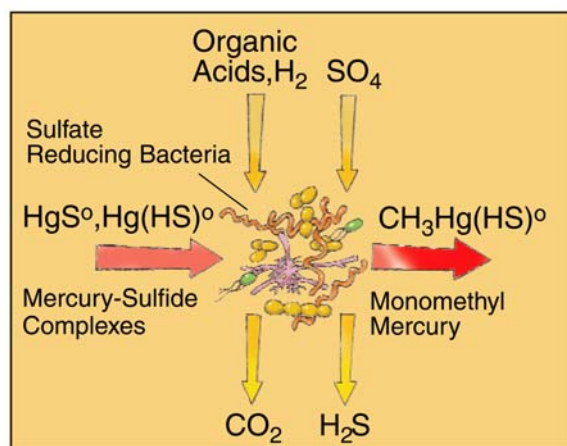

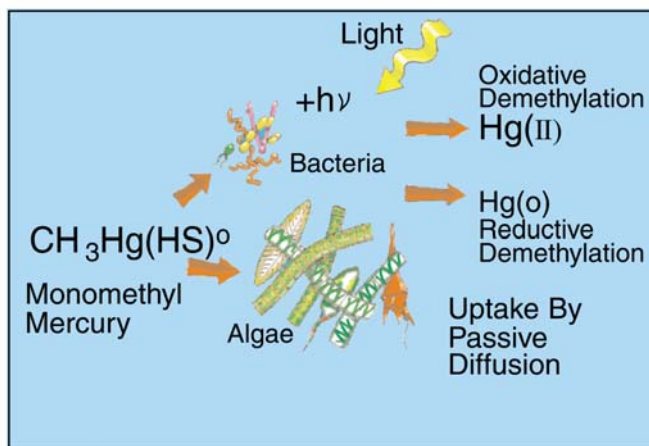Figure 4-5. Mercury methylation reducing bacteria.

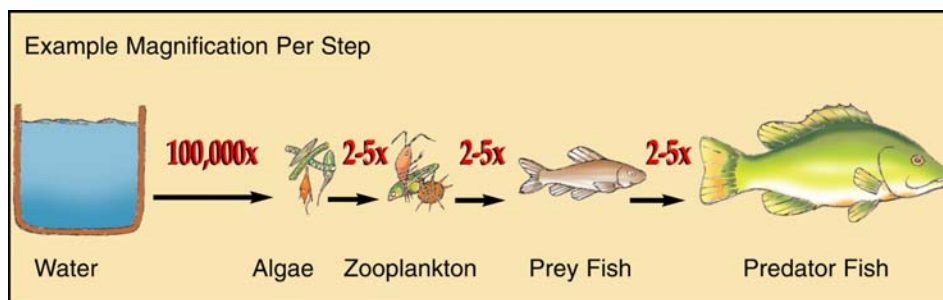Figure 4-6.   Uptake of sulfate-methylmercury

Figure 4-7. Food chain biomagnification of methylmercury.

4.3 MERCURY BEHAVIOR IN GUADALUPE RIVER WATERSHED RESERVOIRS: KNOWNS AND UNKNOWNS

Reservoirs in the Guadalupe River Watershed are characterized by relatively deep water, with well-mixed conditions in the wet season and with stratification and low dissolved oxygen in deeper layers in the dry season. The generally low outflows lead to efficient settling of sediments entering the reservoirs. This is an important pathway for removal of mercury because most of it is strongly associated with the particulate phase. The low dissolved oxygen concentration creates conditions that are likely to solubilize mercury and enhance methylmercury production. As a result of these conditions and processes, the reservoirs are net removers (sinks) for total mercury, but facilitate the production of methylmercury, the form that most readily bioaccumulates.

The general behavior of mercury in reservoirs within the watershed can be inferred from the extensive studies of mercury behavior in lakes. The following processes need to be considered:

- Settling of mercury associated with inorganic and organic particles, and consequent burial in sediments

- Solubilization of historic mercury from sediments, from suspended inorganic particles in the water column, and release from organic particles in the water column

- Complexation of dissolved mercury inputs with dissolved organic carbon, thereby minimizing adsorption and removal by settling particles

- Methylation of dissolved mercury, with the net production of methylmercury being the primary pathway for bioaccumulation

- Loss of methylmercury by biological and photochemical demethylation, loss of inorganic mercury by reduction to Hg(0), and loss from the water column by volitilization

Although all of the processes above are important, by far the greatest research attention has been devoted to the production of methylmercury in the water column and at the sediment-water interface. Methylmercury is a by-product of the activity of sulfate reducing bacteria (Compeau and Bartha, 1985), several different strains of which are found in nature (King et al., 2001). Methylation can occur wherever sulfate reducing bacteria are active, although the hypolimnion and the upper few centimeters of the sediment appear to be the most important zones (e.g., Watras et al., 1995; Gilmour and Riedel, 1995; Bloom et al., 1999; Hines et al., 2000).

For mercury to be methylated, it must first be available in the dissolved form through solubilization from inorganic particles and remineralization from organic particles (Henry et al., 1995, Paquette and Helz, 1997, Benoit et al, 1999). In the water column where sulfate reduction takes place, mercury in the dissolved phase exists primarily as aqueous complexes with ligands such as sulfide and natural organic matter (the solubility of the dissociated Hg^{2+} is negligible compared to the complexed and adsorbed forms). Recent experimental and field studies have led to the hypothesis that the uncharged mercury-sulfide complexes (HgS^0 and $Hg (SH)_2^0$) are the species most likely to be taken up by bacteria and methylated (Benoit et al., 2001), although the potential uptake of other aqueous complexes of mercury by bacterial cells has also been proposed (e.g., Golding et al.,2002; Kelly et al., 2003). Limited data indicate that there is a range of sulfate concentrations over which methylation is stimulated, and concentrations greater than or less than this range tend to suppress methylation by formation of sulfides (Gilmour et al., 2003). In addition to sulfate and sulfide concentrations, the overall behavior of mercury in the water column is also influenced by site-specific conditions including productivity, water temperature, suspended solids, extent of light penetration, pH, alkalinity, dissolved oxygen, dissolved organic carbon, other inorganic anions, and extent of anoxic conditions in the water column or bottom sediments.

4.3.1 RESERVOIR DATA SPECIFIC TO GUADALUPE RIVER WATERSHED

Total mercury concentrations in reservoirs in the Guadalupe River watershed have been measured in a synoptic survey conducted as part of the mercury TMDL (Tetra Tech, 2003d). These measurements characterize mercury concentrations in three parts of the reservoirs: 1) near the surface, 2) in the upper portion of the hypolimnion, at a depth of about 10 feet below the thermocline, and 3) the deeper waters of the hypolimnion. The measurements that represent the deeper portion of the hypolimnion were collected just downstream of the reservoir outlets.

The total mercury and methylmercury concentrations from these three parts of the reservoirs were summarized previously in Figure 3-2a. The ranges of the values are given in Tables 4-1 and 4-2. All Synoptic Survey data are summarized in Chapters 2 and 3 of this report.

Table 4-1
Range of Total Mercury Concentrations (ng/l) in Four Reservoirs

Sampling Location	Guadalupe	Almaden	Calero	Lexington
Surface	10.6 - 20	5.6 - 6.8	1.6 - 2.4	1.4
Hypolimnion 10 feet below thermocline	7.6	5.9	3.4	2.2
Deeper Hypolimnion	18.9	7.5	3.8	12.8

Table 4-2
Range of Unfiltered Methylmercury Concentrations (ng/l) in Four Reservoirs

Sampling Location	Guadalupe	Almaden	Calero	Lexington
Surface	1 - 4.6	1.8 - 3.3	0.8 - 1.1	0.6
Hypolimnion 10 feet below thermocline	2.9	2.3	3.1	1.3
Deeper Hypolimnion	8.3	4.3	2.8	0.8

The Synoptic Survey data give insight on the behavior of mercury during mid-summer, particularly in the upper portion of the Guadalupe River Watershed. In essence the data can be summarized as follows.

- In the surface and upper portion of the hypolimnion, total mercury concentrations between 5.6 and 20 ng/l were measured in the two reservoirs nearest to the New Almaden Mining District (Guadalupe and Almaden Reservoirs)

- Lower total mercury concentrations were measured in the surface and upper portions of the hypolimnion in the other two reservoirs, Lexington and Calero (between 1.4 and 3.4 ng/l). Lexington Reservoir was selected as a control for the synoptic survey. No mercury mining is known to have occurred in its watershed.

- Total mercury concentrations at the outlets of Almaden and Calero Reservoirs are similar to concentrations measured in upper portion of the hypolimnion.

However, the total mercury concentration at the outlet of Lexington Reservoir was more than five times the concentrations measured in the reservoir (12.8 ng/l vs. 2.2 ng/l), and total mercury at the outlet of Guadalupe Reservoir was more than twice what was measured in the reservoir (18.9 ng/l vs. 7.6 ng/l).

Methylmercury (unfiltered) concentrations in the reservoirs, on the other hand, exhibited a narrower range of concentrations:

- Methylmercury concentrations in the epilimnion ranged from 1 to 4.6 ng/l in Guadalupe and Almaden Reservoirs, 0.8 to 1.1 ng/l in Calero Reservoir, and was 0.6 ng/l in a single sample at Lexington Reservoir.

- Although the reservoirs are expected to have greater methylation rates in the hypolimnion due to anoxic conditions, large differences in methylmercury concentrations were not observed between the surface and hypolimnion measurements at Almaden Reservoir.

- Calero Reservoir did show a difference in total methylmercury concentrations between deep and shallow layers. Methylmercury levels in Calero Reservoir were approximately three times higher in the hypolimnion than in the epilimnion layer (3.1 ng/l vs. 1.1 ng/l)

- Methylmercury concentrations in the samples from near the reservoir outlets, representing the deeper portion of the hypolimnion, were substantially higher than the values measured at the surface or upper hypolimnion at Guadalupe Reservoir (8.3 ng/l vs. 2.9 ng/l) and Almaden Reservoir (4.3 ng/l vs. 2.3 ng/l). Methylmercury concentrations were more similar throughout the water column at Lexington Reservoir. Reservoir-outlet methylmercury concentrations in Lexington were much lower than methylmercury concentrations measured from the outlets of the other three reservoirs (0.8 ng/l vs. 2.8 to 8.3 ng/l).

Sampling of reservoir sediments was reported in 1992 (WCC). Based on this survey, Almaden Reservoir had the highest sediment total mercury concentrations (average 27 mg/kg, n = 8), followed by Guadalupe Reservoir (2.4 mg/kg, n = 2), Calero Reservoir (0.6 mg/kg, n = 28), and Lexington Reservoir (0.3 mg/kg). These averages may not adequately reflect current surficial sediment concentrations; they are based on a small number of measurements at various times, using different methods, and by different investigators 13 to 32 years ago.

4.3.2   CURRENT UNDERSTANDING OF MERCURY BEHAVIOR IN RESERVOIRS PERTINENT TO TMDL

The reservoirs closest to the historic mercury mines have the highest concentrations of total mercury in their waters. It is very likely that sediment runoff from mine wastes and seepage through abandoned mines leads to the higher mercury concentrations in the Guadalupe and Almaden Reservoirs. Although the total mercury concentrations measured at Guadalupe and Almaden Reservoirs are below The California Toxic Rule (CTR) human health criterion of 51 ng/l total mercury, some of the measured concentrations are high relative to background conditions[1,2]. Understanding mercury levels in Calero and Lexington Reservoirs, that are thought to not be impacted by mercury mines, is important for developing an understanding of the concentrations of total mercury and methylmercury that can be achieved in all reservoirs in the watershed.

A review of total mercury concentrations in the epilimnion, the shallow hypolimnion, and the deeper hypolimnion (Table 4-1) indicates that (1) in Guadalupe and Almaden Reservoirs the epilimnion concentrations are nearly the same as the shallow hypoliminion concentrations, (2) in Lexington and Guadalupe Reservoirs, the deeper hypolimnion concentrations are clearly higher than the epilimnion concentrations. The second finding is supportive of a mechanism leading to dissolution of sediments (in the presence of sulfides, for example). However the first finding suggests that there may be other shallower sources of mercury in the water column as well. Possible sources are the epilimnetic sediments or mercury inflows during winter. A more complete explanation of this behavior is required in future work.

The methylmercury concentrations measured in all four reservoirs (Table 4-2) are high relative to expected values in freshwater systems. Understanding the high methylmercury concentration levels in Calero Reservoir (0.8 to 3.1 ng/l), is especially important to understanding the processes that must be controlled to reduce methylmercury production throughout the watershed.

Based on water quality data measured during the synoptic survey, it is likely that the productivity of the reservoirs is sufficient to produce anoxic conditions in the deeper waters, leading to conditions that methylate mercury. The finding of relatively high methylmercury levels in the shallower waters of the reservoirs, even under poorly-

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[1] For the purpose of these discussions, the following criteria are used to define high and low concentrations. In water, high concentrations are those over 1 ng/l for methylmercury and over 10 ng/l for total mercury. Low concentrations are those below 0.2 ng/l for methylmercury and below 2 ng/l for total mercury. For sediment concentrations, high total mercury concentrates are those above 2 mg/kg and low concentrations are those below 0.5 mg/kg.

The results of the USGS National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients (Krabbenhoft et al, 1999) provide a basis of comparison for the mercury concentrations. The median concentration of methylmercury in 106 samples was 0.06 ng/l. The median total mercury concentration in water was 2.28 ng/l. The median sediment mercury concentrations in the USGS study were 0.046 mg/kg.

mixed conditions, is indicative of significant methylmercury production in the
epilimnetic zone, probably in the sediments.

The methylmercury that forms in the reservoirs is (1) taken up by algae and is
transferred to higher trophic levels through the food chain, (2) transported
downstream, or (3) gradually demethylated and possibly volatilized via biotic and
abiotic pathways.

4.3.3 HYPOTHESES AND DATA REQUIREMENTS: RESERVOIRS

The USGS National Pilot Study of Mercury in Fish (Brumbaugh et al, 2001) used
data from106 sites nationwide to develop a predictive relationship between
methylmercury concentrations in water and concentrations in fish tissue. It was
found that methylmercury concentrations greater than 0.12 ng/l in the water were
associated with mercury concentrations greater than 0.3 mg/kg in age-3 freshwater
piscivorus fish. Based on this information, it is likely that the levels of
methylmercury concentrations measured in all four reservoirs in the Guadalupe River
Watershed are sufficiently high to cause the ambient methylmercury water quality
criterion for fish (0.3 mg/kg in tissue) to be exceeded.

Methylmercury production in the reservoirs has been shown to be significant. It is
therefore important to identify the source for methylmercury production, the primary
locations of methylmercury production, and the fate of methylmercury produced in
the reservoirs. This information will be critical to establishing the ability to control
and predict the changes in reservoir methylmercury concentrations. It is with this
goal in mind that the following three hypotheses have been developed to guide future
data collection efforts. [2]

Reservoir Hypothesis 1
*Reduction of total sediment mercury will cause a proportional decline in
methylmercury concentrations.*

A possible source for mercury in the water column of the reservoirs in the dry season,
when most of the methylation takes place, and when there are no surface-water
inflows, is through solubilization and/or suspension of sediments. Mercury that has
been solubilized may be methylated. In addition, the upper sediment layer may be a
source of methylmercury production. For these reasons, it may be hypothesized that

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[2] The Maximum Contaminant Level (MCL) for mercury is 2 ppb (2,000 ng/l). The MCL is the U. S. Environmental
Protection Agency's enforceable standard for drinking water. The difference between the MCL and the California
Toxic Rule human health criterion (51 ng/l) is related to the potential exposure pathway assumed in the development
of these two standards. The CTR value assumes the uptake and bioaccumulation by aquatic organisms and the
eventual ingestion by humans as fish tissue. The MCL value assumes ingestion of drinking water and is based on
the lowest level to which water systems can reasonably be required to remove mercury from drinking water.

reduction of total sediment mercury may lead to a reduction of methylmercury production.

It is possible that the dissolution of sediment mercury and the methylation of dissolved mercury are both described by plateau-type relationships, such as shown in Figure 4-8. There may be a range of concentrations over which sediment mercury and water column methylmercury are proportional, and a range of concentrations where the methylmercury concentrations are unrelated to the sediment concentrations. This may be a result of a limitation, as yet unknown, in the dissolution or methylation of mercury. The initial conditions, i.e., whether we are at location A or B or C in Figure 4-8, may determine the effect of changing sediment mercury on water column methylmercury concentrations. A similar relationship was found by Krabbenhoft et al. (1999).

An alternative hypothesis is that dissolved mercury in the water column, from sources other than the sediments, is the primary source of mercury being methylated. Then changing sediment concentrations would have little effect on methylmercury production. The water-column concentration of mercury may be more important than the sediment-mercury concentration in the event that newly supplied mercury, in runoff and deposition, is more bioavailable than sediment mercury. There is some evidence in the literature that "new" mercury is more bioavailable than "old" mercury (Gilmour et al., 2003). Whether this is quantitatively significant in the Guadalupe Watershed remains to be seen. It is also possible that both the dissolved mercury inputs to the reservoirs and the solubilization of sediment mercury are quantitatively important.

Data Needed: More detailed sediment mercury data from reservoirs are needed with co-located methylmercury measurements. Experimental (field or lab) studies should be conducted to identify methylmercury concentrations as a function of total sediment mercury concentration. Measurement of methylmercury production rates throughout the epilimnion and hypolimnion are needed.
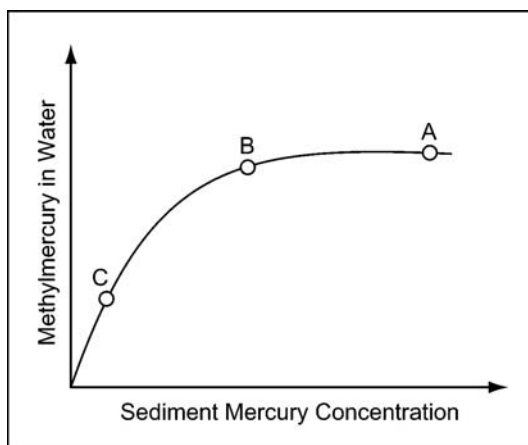

Figure 4-8.
Hypothesized relationship between sediment mercury and methylmercury concentrations in water

Reservoir Hypothesis 2

Methylmercury accumulated and/or produced in the epilimnetic zone of the reservoirs during the summer stratification period is significant and makes an important contribution of mercury to the food chain.

The average methylmercury concentrations in the surface water samples of Guadalupe Reservoir (3.3 ng/l) were approximately equivalent to the methylmercury concentration (2.9 ng/l) measured in the upper part of the hypolimnion (Table 4-2). A similar pattern was observed at Almaden Reservoir, where the average methylmercury concentration in the epilimnion and that measured in the upper part of the hypolimnion were both 2.3 ng/l. Similar behavior was also observed for total mercury in Guadalupe and Almaden Reservoirs. Since a moderately strong thermal gradient exists between the hypolimnion and epilimnion, the transport of total mercury and methylmercury from the hypolimnion to the epilimnion is likely limited.

Data Needed: Temporal characterization of the distribution of total and methylmercury in the reservoirs before and during the period of stratification is needed. Measurement of methylmercury production rates and rate constants in both the epilimnion and hypolimnion are needed.

Reservoir Hypothesis 3

A significant quantity of the methylmercury produced in the reservoirs during the warm season may be transported to creeks downstream.

Methylmercury is produced most rapidly during the warm season (July, August, and September). Outflows from the reservoirs during this period appear to contain high methylmercury concentrations. The two reservoirs with the highest methylmercury levels, Almaden and Guadalupe, also have relatively low storage capacities (1,586 and 3,223 ac-feet, respectively). At typical summer flows of 4-6 cfs, over a 90-day period, half to one-third of the volumes of these reservoirs, and a proportional amount of methylmercury, can flow out. After the warm months, the reservoirs become well mixed during fall turnover and methylmercury concentrations likely begin to decrease.

Data Needed: More temporal data on methylmercury concentrations in the reservoir and the outflows are needed to constrain mass balances of the production, downstream transport, and demethylation of methylmercury.

4.4   MERCURY BEHAVIOR IN CREEKS: KNOWNS AND UNKNOWNS

Creeks that flow into the reservoirs are characterized by steep energy gradients and highly variable or intermittent flows. Creeks immediately downstream of the four major reservoirs exhibit lower variability in the flow, especially in summer where reservoir discharges form a major portion of the total flow. Most of the water, and by association, sediment transported by creeks occurs during the wet season (generally November through April). Mercury is strongly associated with particles, and total

mercury loads transported by creeks are closely correlated with sediment transport. The role of sediment transport is important in all watersheds, but is particularly important in basins such as Guadalupe River that have mine wastes and naturally high mercury deposits. High flow events can cause erosion of stream banks and scouring of sediment. Because sediment transport is seasonal, so too are mercury loads delivered to water bodies. For adequate quantification of loads, there needs to be a relatively high frequency of measurement of mercury concentrations in streams under different flow regimes.

The correlation of mercury and sediments transported under high flow events has been noted in many studies. Large differences between low and high flow sampling have been measured in mountain streams draining areas with mines (e.g., Domagalski, 1998; Whyte and Kirchner, 2000). At a creek downstream of the Gambonini Mercury Mine in California, flow, suspended solids, and mercury were measured on 18 dates over a 59-day period of the rainy season. Over 75 percent of the total mercury load was released in storms on five days, and 40 percent was discharged during a single storm event over a 28-hour period. This study illustrated the importance of stream erosion and transport of sediment during large storms, particularly when mine wastes are present in or near the stream channel.

Quantifying these loads requires storm event sampling, which can be logistically challenging. But, if storm events are not properly considered in load calculations, projected loads to receiving water bodies will likely be seriously underestimated.

4.4.1 CREEK DATA SPECIFIC TO GUADALUPE RIVER WATERSHED

Dry season total and dissolved mercury and unfiltered methylmercury data from the major creeks in Guadalupe River Watershed has been reported earlier (Technical Memorandum 2.2; Tetra Tech, 2003d). Total mercury concentrations are high (see footnote on page 4-10) in the upper reaches of the watershed that drain the historic mining area, 109-191 ng/l, and are significantly lower at the outlets of the reservoirs in the mining area, 7.5-19 ng/l. Total mercury in most creeks downstream of reservoirs in the watershed, i.e., Guadalupe, Alamitos, and Calero Creeks, appear to initially increase with distance downstream (18-570 ng/l), with Los Gatos Creek being an exception. Dissolved mercury concentrations in the creeks do not show consistent changes with travel distance. Both filtered and unfiltered methylmercury concentrations, on the other hand, show a distinct drop-off with distance in all of the creeks (see Figure 4-9).

Sediment mercury concentrations in the creeks show a significant and consistent decline with travel distance downstream (Tetra Tech, 2003d). Concentrations are greatest in the two major creeks downstream of the mining areas, Guadalupe and Alamitos. Guadalupe Creek values decrease from 125.3 to 21.9 mg/kg, and Alamitos Creek values decrease from 168.5 to 19.7 mg/kg. Methylmercury is also seen in the sediments although as a small percentage of the total mercury, (often lower than 0.1%). High sediment concentrations of methylmercury, greater than 0.005 mg/kg, generally occur in areas with moderate to high total mercury concentrations.

Comparative sampling of creeks in the Guadalupe River Watershed under low and high flow conditions has been also been performed by two groups (Tetra Tech, 2000 and 2001; Thomas et al., 2002) although the data are spatially less extensive than the Synoptic Survey described above. Data collected by Tetra Tech (2000, 2001) during the dry and wet season along a short reach of Guadalupe Creek (3 miles downstream of the reservoir) show that, on average, the total mercury concentrations in water increased by more than three times between the dry and wet seasons (from 12-145 ng/l in the dry season, to 64-223 ng/l in the wet season). Methylmercury, on the other hand, did not show a strong seasonal trend and was found to be slightly higher in dry summer sampling (0.3 to 1.6 ng/l) than in the wet winter sampling (0.25 to 0.53 ng/l). In both the dry and wet season sampling of Guadalupe Creek, it was found that total mercury decreased with distance downstream, although dissolved mercury levels remained fairly constant. Over the same reach, dissolved and total methylmercury, on the other hand, showed a decrease with distance in the dry season, and a slight increase with distance in the wet season. In the Thomas et al. (2002) study, data were collected in Guadalupe River in October 2000 for base flow conditions, and for flows following a two-day rain event. Total mercury concentrations were slightly higher during the high flow event, but because the flow rate increased by a factor of 10 from the base flow, the loads of mercury transported were substantially greater during high flow conditions. The two-day rain event sampled by Thomas et al (2002) contributed almost 75 percent of what the base flow would produce for the entire month of October 2000. Stream sediment data from the Guadalupe River are supportive of the spatial trends observed in the water column: sediment total mercury concentrations decrease with distance from mercury sources.

4.4.2 CURRENT UNDERSTANDING OF MERCURY BEHAVIOR IN CREEKS PERTINENT TO TMDL

Mercury is transported by streams in particulate and dissolved forms. During the transport, some of the mercury is removed by settling of particles, some of the inorganic mercury is methylated, and methylmercury present in the flowing water may be lost through removal mechanisms, including biological uptake, photocatalyzation, and biotic demethylation. The rates, mechanisms, and seasonality of these processes are not well known in the Guadalupe River Watershed.

Preliminary data indicate that the behavior of creeks in the wet season is very different from that in the dry season. In the wet season, creeks act as transporters of sediment-bound and dissolved mercury from upper reaches to lower reaches, and mercury methylation processes are thought to be relatively insignificant due to the higher flows and lower temperatures. In the dry season, sediment deposits in some creek reaches downstream of the mined areas, but above the confluence with Guadalupe River, serve as mercury sources to the flowing water, and total mercury concentrations increase with distance downstream.
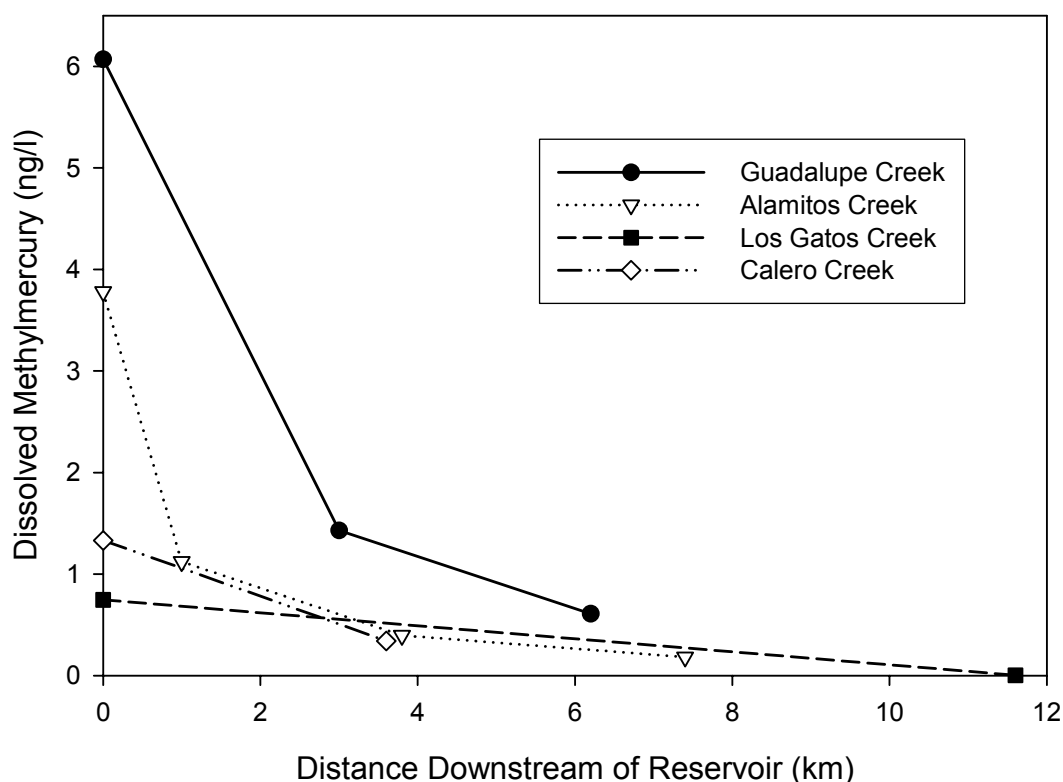
Figure 4-9. Dissolved methylmercury in creeks downstream of the reservoirs

4.4.3 HYPOTHESES AND DATA REQUIREMENTS: CREEKS

Creek Hypothesis 1

Most of the mercury is transported in the wet season.

During the wet season, mercury-containing runoff from mine-waste sites enters the creeks in the upper watershed, many of which have flow only during the wet season. The peak flows in the creeks are large, accompanied by high sediment concentrations and high total mercury concentrations. Mercury is transported largely in particulate form, but a significant amount may be dissolved. Individual storms can be responsible for transporting a large fraction of the annual load. However, much of the sediment-bound mercury may be trapped downstream in Almaden Lake and the drop structures in normal wet-season flows.

Data Needed: Because the peak flows only last for a short while and mercury concentrations are highly variable over a time-scale of hours, intensive synoptic sampling is needed to capture the flows and mercury concentrations following one or more large winter storms.

Creek Hypothesis 2

Methylmercury discharged from reservoirs is significantly removed or demethylated in the creeks.

Synoptic survey data show that methylmercury concentrations decrease with travel downstream in Guadalupe, Almaden, Calero, and Los Gatos Creeks in the dry season. It is not known whether the discharge of dissolved mercury and methylmercury from the reservoirs and the decline in concentrations is similar during the cooler, wetter months of the year. This information is needed to understand the movement of bioavailable mercury from the upper watershed to the lower reaches, and to evaluate the downstream benefits, if any, of controlling mercury methylation in the upper watershed.

Data Needed: Measurement of methylmercury concentrations exiting from reservoirs and in the creeks during the wet months using an approach similar to that used in the Synoptic Survey.

4.5   MERCURY BEHAVIOR IN GUADALUPE RIVER: KNOWNS AND UNKNOWNS

Flow in Guadalupe River, the stretch south of the drop structure above Blossom Hill Road to South San Francisco Bay, is generally similar to that of the creeks in the watershed, but with the following differences: a portion of the river is being channelized, the river flows through a developed, urbanized area, the slope is much lower than in the upper reaches of the watershed, and the lowermost portion of the river is tidally influenced. Flows are variable, and mercury transport, as in the creeks, is expected to occur predominantly in the particulate phase during high flows.

4.5.1 DATA SPECIFIC TO GUADALUPE RIVER

A limited number of water column measurements of mercury in Guadalupe River have been reported. In July, 2003 one station near Blossom Hill Road was sampled during the synoptic survey for the TMDL. Total and dissolved mercury concentrations were both fairly high, 105 ng/l and 8 ng/l respectively, but the methylmercury concentration was relatively low, 0.3 ng/l. Data in the lower Guadalupe River have also been reported by Thomas et al. (2002). Downstream of the confluence with Los Gatos Creek, the total mercury concentration during baseflow in October, 2000 was 26.2 ng/l. Following a storm later that month, however, these concentrations increased sharply to 138.6 ng/l during peak flow, and decreased to near baseflow concentrations as streamflow declined (Figure 4-10). Total mercury concentrations further downstream, in the tidally influenced portion of the river/Alviso Slough, were 86.4 ng/l under baseflow conditions and increased slightly to 98.6 ng/l after the storm. It is unclear whether there was a concentration spike at Alviso Slough during the storm that was not sampled by Thomas et al. 2002. Conaway et al. (2003) also sampled water column concentrations at Guadalupe River/Alviso Slough five times (February, 1999; April, 1999; July, 1999; February, 2000; and July, 2000). Total mercury concentrations varied from 17.6 ng/l to 70 ng/l,

with the highest value measured in February, 1999. Methylmercury values varied from 0.16 to 0.3 ng/l.

Sediment concentration data from Guadalupe River exhibit a complex pattern due partly to construction and channel realignment. Data obtained from SCVWD show that sediment mercury values just south of Almaden Lake, i.e., the area downstream of the creeks draining the historic mining district, are high (about 42 mg/kg) but diminish rapidly within 5 miles downstream to about 0.4 mg/kg. There is another zone of moderately high concentrations 4 to 10 miles downstream (concentrations 2.4 to 7.9 mg/kg). Beyond this distance, corresponding to river mile 11 from the Bay, concentrations decrease continuously from about 5-8 mg/kg to about 0.4 mg/kg near the confluence of the Guadalupe River/Alviso Slough with South San Francisco Bay. Sediment concentrations in Guadalupe River measured by Thomas et al. (2002) were 2.8 mg/kg at Almaden Expressway, with 0.1 percent being methylmercury. Conaway et al. (2003) measured sediment mercury concentrations twice in the Lower Guadalupe River/Alviso Slough (July, 1999 and July, 2000) and these values were between 0.2 to 0.7 ppm with 0.1 to 2 percent methylmercury.
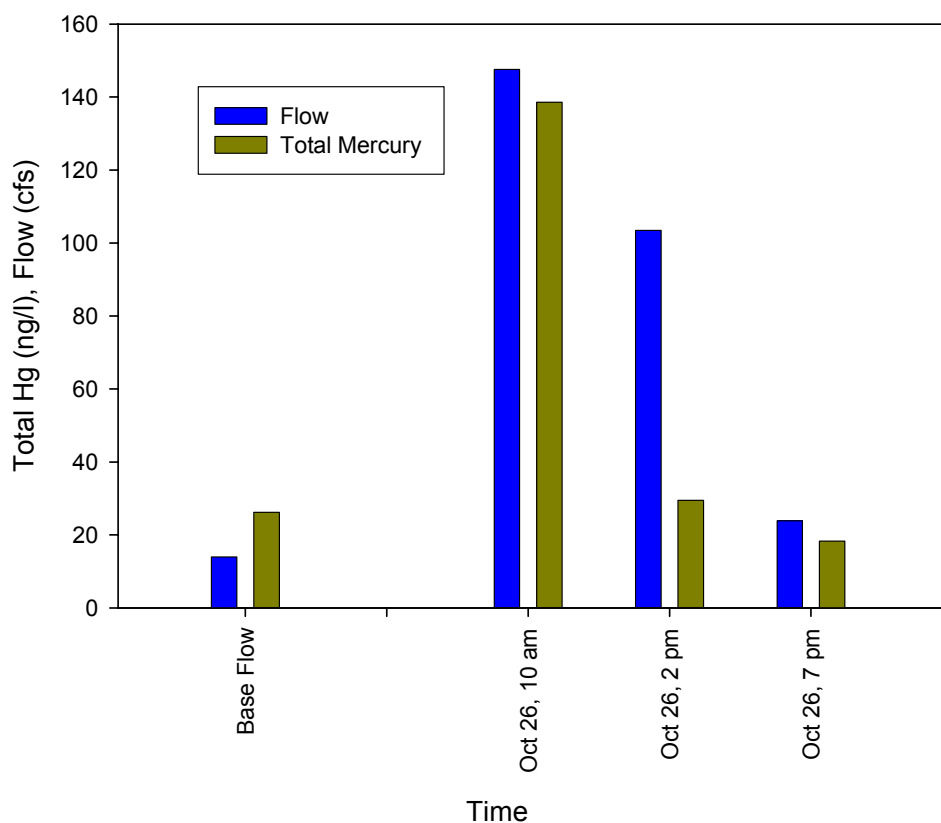

Figure 4-10   Flow and Hg on Guadalupe River downstream of confluence with Los Gatos Creek, (Thomas et al., 2002)

4.5.2 CURRENT UNDERSTANDING OF MERCURY BEHAVIOR IN GUADALUPE RIVER PERTINENT TO TMDL

The behavior of total mercury in Guadalupe River can be conceptualized in two ways: (1) as a receptacle and conveyor of mercury from the upper reaches, with some attenuation and transformation, and/or (2) as having an independent source of mercury because of mine-waste deposits in its sediments and banks. If the first conceptualization is appropriate, then Guadalupe River can be expected to remove total mercury and methylmercury with travel distance in the dry season, and transport sediment-associated mercury during high flows in the wet season. If the second conceptualization is appropriate, however, then mercury processes in the upper watershed, are isolated by reservoirs and Almaden Lake, and have a minimal influence on mercury in the river; what dictates concentrations and downstream transport in the river is the mercury in the stream banks, a result of prior transport. It is possible that actual mercury behavior is best described by a combination of the two conceptualizations. Remedial approaches for the lower Guadalupe River will require a better understanding of mercury behavior there. For example, removal of mercury-rich sediment from the stream banks would likely be most effective if it is shown that the second conceptualization best represents mercury behavior.

Because of the ongoing modifications of the lower Guadalupe River, its potential to methylate mercury may be significantly reduced. Thus, the lower river might be expected to behave like the creeks, where methylmercury concentrations decrease with travel distance.

4.5.3 HYPOTHESES TO BE TESTED: GUADALUPE RIVER

River Hypothesis 1

The lower Guadalupe River bank sediments are a significant source of mercury during the wet season.

In general, total mercury concentrations decline with travel distance along streams because of the settling of particulates. But during high flows, stream width is greater, and banks are subject to erosion. Because the stream banks contain high concentrations of mercury, these banks can become a source of mercury to the river. To the extent this occurs, removal of bank deposits and sediments with elevated mercury may be an effective means of reducing downstream loads.

Data Needed: Characterization of sediment and bank mercury concentrations at selected river cross-sections. Determination of the extent to which banks and sediments are scoured and eroded.

River Hypothesis 2

Under present conditions sediment-borne mercury in the Guadalupe River does not originate from the upper watershed.

Much of the sediment mercury from the upper watershed is retained in impoundments, including Almaden Lake, and the concentrations of particulate mercury flowing into the Guadalupe River are much lower than those in the upper watershed. Suspended sediments measured in Guadalupe River either originate mostly in the lower watershed or are eroded from the river channel.

Data Needed: Measurements of total suspended sediment and total mercury in the upper watershed and Guadalupe River during low and high flows, especially flows associated with large winter storms.

River Hypothesis 3

Guadalupe River is a net sink for methylmercury.

Although some methylation of mercury may occur, on a net basis, more methylmercury is lost from the creeks of the Guadalupe Watershed through demethylation, adsorption and sedimentation, or volatilization, than is generated within them as shown by the Synoptic Survey. We expect the Guadalupe River to behave similarly.

Data Needed: Unfiltered methylmercury concentrations along the Guadalupe River during low and high flows.

4.6   MERCURY BIOACCUMULATION AND NUMERIC TMDL TARGETS

The listing of waterbodies within the Guadalupe River watershed as impaired was based, in part, on the Office of Environmental Health Hazard Assessment (OEHHA) posting a public health advisory for Guadalupe Reservoir, Calero Reservoir, Almaden Reservoir, Guadalupe River, Guadalupe Creek, Alamitos Creek, and the associated percolation ponds along the river and creeks (OEHHA, 2003). The OEHHA advisory states that, "because of elevated mercury levels in fish, no one should consume any fish taken from these locations."

The importance of fish mercury concentrations in the impairment decision, and the fact that the ambient water quality criterion for methylmercury is expressed in terms of fish tissue concentrations [0.3 mg/kg (ppm), U.S. EPA, 2001], make tissue concentration a strong candidate for a numeric target for use in the Guadalupe Watershed TMDL. The key questions that must be addressed are:

- What is the relationship between fish tissue concentration and mercury concentrations and mercury loading to the waterbodies?

- Can a quantitative relationship be developed between fish tissue concentrations and mercury load reductions that would serve as a basis for the TMDL linkage analysis, i.e., determining what specific actions will result in achievement of the relevant water quality standards.

4.6.1 MERCURY BIOCONCENTRATION AND BIOACCUMULATION IN FISH

Methylmercury typically constitutes a very small fraction of the total mercury in aquatic ecosystems (typically < 1% in sediments and the water column), but it is the critical form or species of Hg that is incorporated into and magnified in the food chain. In fact, in fish, methylmercury accounts for about 95 percent of the total mercury in the muscle tissue (Grieb et al., 1990; Bloom, 1992). The assimilated mercury is distributed throughout the tissues and organs of the fish, but a large portion of the methylmercury eventually relocates to skeletal muscle where it becomes bound to sulfhydryl groups and sulfide and disulfide linkages associated with the muscle protein.

A simplified representation of bioconcentration and biomagnification of methylmercury in the aquatic environment is shown in Figure 4-7. Initially, mercury is bioconcentrated from water into planktonic algae cells. Bioconcentration is quantitatively defined as the log of the ratio of the concentration of mercury in the algal biomass to that in the water:

$$BCF_{plankton} = log\ (C_{plankton}/C_w)$$

where $BCF_{plankton}$ is the bioconcentration factor for phytoplankton, and $C_{plankton}$ and C_w are Hg concentrations in phytoplankton and water.

The bioconcentration factor for mercury in phytoplankton can be on the order of 5 to 5.5. That is, phytoplankton concentrations are about 100,000 to 300,000 times water concentrations (Lindqvist et al., 1991; Watras and Bloom, 1992; Mason et al., 1996).

The corresponding bioaccumulation factors between phytoplankton and zooplankton or benthos and fish are small relative to the large increase in methylmercury concentrations between the water and plankton. As a rule of thumb, the bioconcentration values for methymercury increase by about 0.5 log units (a factor of three times) per trophic level after the initial uptake by phytoplankton. The concentration of methymercury in predatory fish tissue can be more than 3 million times the concentration in water.

Dietary uptake is the dominant pathway for methymercury accumulation in fish. Fish have been estimated to assimilate from 65 to 80 percent of the methymercury present in their food (Wiener et al., 2002). Not only is mercury readily assimilated, it is only slowly eliminated. This results in increasing methylmercury in fish as a function of

age, size, and trophic level (Gray, 2002). Figure 4-11 shows the typical relationship between mercury concentration and the size of a particular fish species.
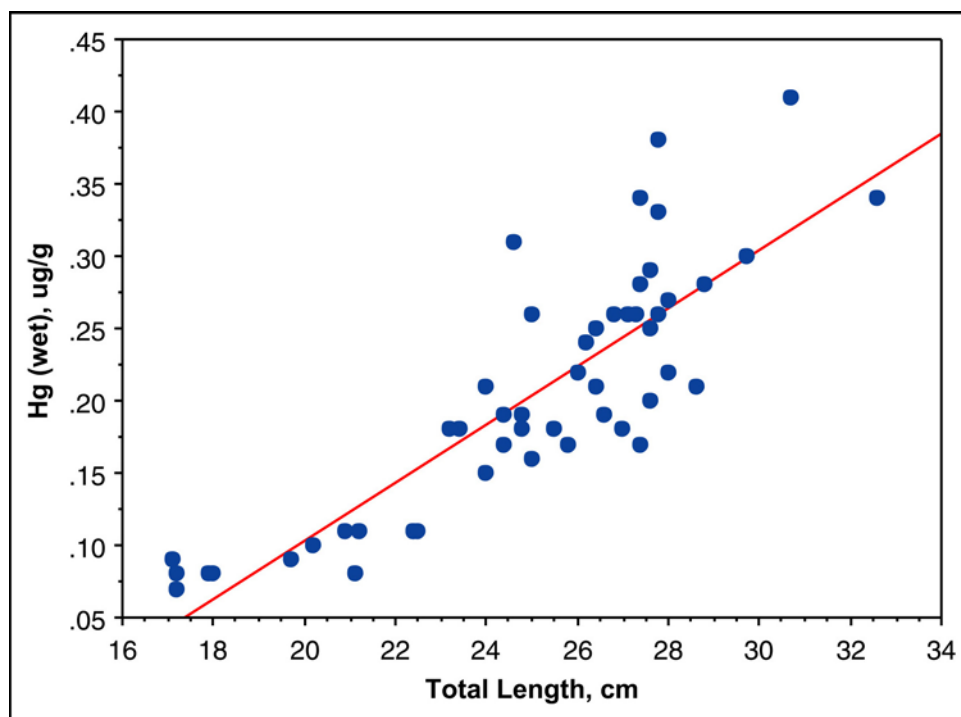

Figure 4-11. Example relationship between fish size (total length) and mercury concentration in muscle tissue.

4.6.2 CURRENT UNDERSTANDING OF BIOACCUMULATION PERTINENT TO TMDL

The relationship between mercury in the aquatic environment and fish tissue is widely accepted, but the level of mercury in fish tissue can be affected by numerous factors including fish species, age of the fish, seasonal characteristics, and the availability of prey items.

In order for fish mercury concentration to be used as an effective numeric target, a linkage must be established between potential methylmercury reductions in the waterbodies and changes in fish tissue concentrations. On a national or regional scale, there are limitations to estimating fish concentrations from methylmercury concentrations in sediment or water. But on a local watershed scale this objective may be more readily achieved. Direct measurements made over the period 1994-2000 have demonstrated concomitant reductions of mercury concentrations in precipitation, lake water, and fish tissue in an intensely monitored seepage lake in northern Wisconsin which receives almost all of its mercury from atmospheric deposition (Watras et al. 2000; Hrabik and Watras, 2002). Mercury deposition decreased by approximately 50 percent between 1994 and 1999, and mercury concentrations in lake waters decreased an average of 40 percent between 1988 and 2000 (Watras et al., 2000). Fish tissue

measurements and statistical modeling indicate that fish mercury concentrations responded with a decrease of between 35 and 65 percent (Hrabik and Watras, 2002).

4.6.3   HYPOTHESIS AND DATA REQUIREMENTS: BIOACCUMULATION

A single bioaccumulation hypothesis addresses the ability to develop numeric targets. Several feasibility issues are also discussed.

Bioaccumulation Hypothesis 1

A predictive relationship can be established between aqueous methylmercury concentrations in the basin waterbodies and mercury concentrations in the fish.

Data Needed: The measurements of mercury and water quality parameters made in the Synoptic Survey demonstrate that an adequate range of mercury concentrations exist in the reservoirs and creeks to test this hypothesis. Additional fish data from the reservoirs and creeks are now needed to determine how fish tissue concentrations of mercury vary with methylmercury concentrations in the waterbodies. Measurements of mercury concentrations in the muscle tissue for several species and different sizes of fish are required from multiple locations in the watershed. The collection of largemouth bass and black crappie samples from Guadalupe Reservoir in May, 2003 (see Chapter 3) indicate that fish from different size ranges can be collected relatively easily from the reservoirs. The analysis of samples from other waterbodies are now needed to make the required comparisons.

A fish-sampling program to detect differences in fish tissue levels is important. The mercury concentrations that have been measured in the sediments and water from the Guadalupe watershed are higher than those reported in other basins, but the available fish data indicate the fish tissue concentrations are high, but are not proportionately high. It will be important to establish the feasibility of detecting changes in the levels of mercury in fish tissue from these relatively unknown fish populations. It will be necessary to determine the numbers of fish that need to be collected to detect various levels of change. Statistical testing methods need to be evaluated prior to establishing monitoring efforts, and statistical power analyses need to be performed using fish data from the initial data collection efforts to quantify the effectiveness of alternative sampling designs.